Optical Studies of Non-linear behaviour of Dye-doped Liquid Crystal Systems

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Abstract

Dye-doped Liquid Crystals (LCs) are very attractive materials for many applications (Optically Addressed Spatial Light Modulators, dynamic holography, all-optical switching) because of their high sensitivity to optical fields, possibility of use in transmission and low cost. The complexity of the physical effects (surface mediated and bulk) which take place in a doped cell when it is illuminated [1-4], hampers the simple engineering of devices. A good understanding of these effects is a primary goal of this research.

A comparison of materials based on temporal and spatial resolution and efficiency is presented. Photorefractive-like effects and various underlying mechanisms are considered.

Keywords: dye-doped, Liquid Crystal, photorefractivity, trans-cis isomerisation, photovoltage.

1 Introduction

Dye-doped NLC were studied by many authors [1-6] as media for various nonlinear effects (self-focusing, stimulated orientational scattering, orientational photorefractivity, real-time holography etc.). Various dyes show optical nonlinearity of disparate origins including trans-cis photoisomerisation [1, 6], surface [4] and ionic effects [3].

It is possible to distinguish between some of these effects on the basis that they occur on different time scales, have different dependency on the cell thickness, grating spacing, cell surface, host material, external fields etc. For example, surface effects are usually on the 1s scale [6], as well as photovoltage generation and spatial charge formation [3]. With some alignment agents some dopant molecules can be adsorbed on the surface producing permanent holograms [3, 4].

We have chosen LC-dopant systems to represent different groups of dopants used by research groups [1-4]. The samples studied are 5-20μm thick planar aligned nematic LC doped with small amounts (0.5 - 1%) of azo dye

Methyl Red, 2,6 azo-substituted anthraquinone dye and Fullerene. No voltage is applied in the first two cases, whilst the effect in C60 doped materials requires an external electric field. Dynamic holographic grating formation is observed under conditions of low power laser light.

In this paper we will concentrate on the mechanisms leading to nonlinearity in the investigated systems.

2 Samples and Measurement Techniques

2.1 Experimental techniques

The holographic grating is recorded using two Ar+ laser beams (λ=514nm) intersecting at a small angle on the sample and forming an interference pattern (fig.1a). The beam from the laser is collimated and expanded to obtain uniform intensity profile, then split by non-polarising beam splitter and directed to overlap on the sample using a mirror. The interference pattern that is formed is a sinusoidal grating and has a spacing of 12.5μm (corresponds to 80 line pairs/mm (lp/mm)). The beams are ensured to be of equal intensity (within 2%) for the best contrast. Weak He-Ne laser beam (λ=633nm, 1mW) is used to read recorded information. Diffracted orders are symmetrical. The first diffracted order is recorded dynamically using a photo-multiplier and oscilloscope as the writing beams are being switched on and off.

Writing beams are polarised along the director axis of the LC, i.e. along the alignment direction of the device. For efficiency measurements the reading beam is also polarised along the alignment direction, and for orientational studies, its polarisation is rotated by 45°.

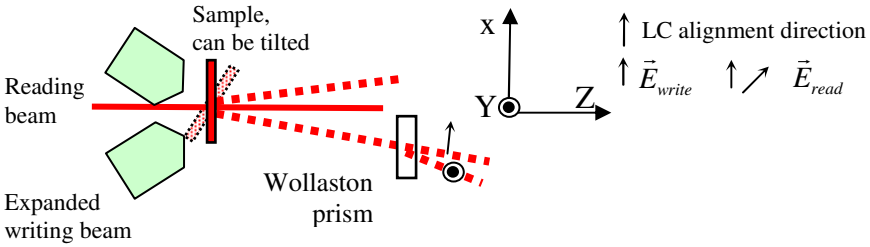

Fig. 1 Experimental setup for holographic grating formation experiment: two-beam interference.

2.2 Samples preparation and materials choice

Cells filled with NLC 5CB doped with 0.5% and 1% wt of dichroic dye DC161 having thickness 5, 9 and 15μm were available (fabricated in 1987). A good planar alignment was achieved by SiOx alignment as confirmed by polarising microscope studies and absorption measurements in polarised light. These devices showed good performance

(diffraction efficiency for holographic gratings at 50mW/cm^2 up to 1%, in 10-100ms regime. This performance is good as compared with our MR and C_{60} doped devices. It is also important to note that no permanent component formation under any circumstances (optical power up to 1W/cm^2, external fields up to 10V) was observed, which is a big advantage for dynamic holography applications.

To understand better the nature of nonlinearity in these devices, possible mechanisms and influence of alignment layer and host material, as well as to research the possibilities of improving their performance by engineering the structure, new devices have been built. These samples consist of two ITO glass slides, usually with a rubbed polyimide layer as an aligning agent. The thickness of new devices is 10, 14 and 20μm. These cells were filled with dye-doped LC mixtures.

We used several commercially available nematic LCs: 5CB, BLO48 and E7 from Merck as host materials.

Host material	Birefringence Δn (at λ=589nm)	Clearing point T_{NI}
5CB	0.18	34^{o}C
E7	0.2246	61^{o}C
BLO48	0.2627	100^{o}C

Table 1. Physical parameters of the host materials used.

We had a number of reasons for choosing these liquid crystals. Firstly, it is interesting to reproduce the already functioning device with the same materials (5CB). Secondly, one would expect larger effect in materials with high dielectric and optical anisotropy (E7 and BLO48). Indeed, the light-induced optical torque in such systems is larger [7], and also the same change in the orientation of the LC molecules will yield higher change in refractive index and hence in the efficiency of the diffracted signal for the materials with higher Δn. Thirdly, a wide temperature range is beneficial for applications, and also allows the influence of critical near-transition temperature behaviour of LC parameters to separated out. And last, but not the least, different chemical compositions of host materials will also allow to be seen whether the effect relies on dye-host interaction and its change upon excitation as in [2].

The alignment agent in dye-doped systems can be very important [3, 4]. It has a defining effect in case ionic and surface effects are involved [5]. To look at the effect the alignment imposes on the samples, planarly aligned devices with obliquely evaporated SiOx, and rubbed PI, PVA, glass and ITO surfaces have been built; to research surface effects, a wedge cell (thickness varying from 0 to 2μm) with hybrid alignment was created; also homeotropic samples have been prepared (using commercially available aligning agents ZLI2222 and HTAB). Testing devices with different alignment agents helps to separate ionic and surface effects from bulk effects. Such separation is based on the

fact that surface effects are very sensitive to the aligning agent while ionic effects are strongly enhanced by using ionic surfactants like HTAB [6].

3 Possible effects and mechanisms in studied systems

Mechanisms that can lead to nonlinearity in dye-doped LC systems can be compiled in a rather long list. We aim to consider all relevant mechanisms and to understand what processes take place in the systems under investigation.

High-power effects

Electrostriction (Brillouin scattering); flows

Both processes require very high optical fields and are usually studied with high-power pulsed lasers. We are working with a laser power too low to observe these effects.

Ionic and charge-related effects

Photovoltaic effect (optical rectification)

Photovoltage is measured dynamically as the expanded uniform beam from the Ar+ laser at λ=514nm impinges on the sample. A shutter with variable switching time is used. We do not register any photoinduced currents or voltages in undoped planar 5CB, BLO48, and planar and homeotropic E7 films. This indicates that the light intensities and wavelengths used are not capable of creating ions in pure materials and that alignment layers used do not introduce many ions into the sample and prevent charge injection from ITO electrodes. While the charge injection from the electrodes and host material influence are eliminated, the observed effects can be solely attributed to the dopant itself.

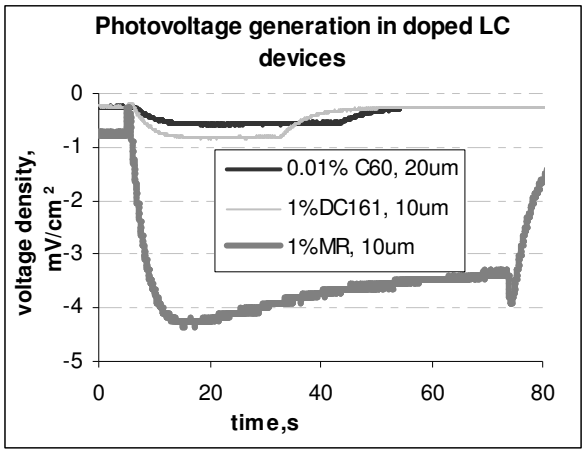

Fig. 2. Generated photovoltage in MR and DC161 doped LC devices. Data for 20um C_{60} doped BLO48 is also given for comparison.

The measurements show small DC fields generated under the influence of light in DC161 samples. MR doped samples show photovoltage generation (as observed previously [3]) and strong dependence on previous illumination history, especially in conjunction with SiOx alignment. C_{60} doped samples also show a small photovoltage, only 0.25mV from the 20μm sample (while 10μm MR doped sample gives 4mV).

Fig 2. illustrates generated photovoltage in samples of same thickness, same alignment (polyimide PI) and same host material (5CB), doped with 1% of MR and 1% of DC161. The dependence for C_{60} doped 20μm PI aligned sample is also shown for comparison. The expanded laser beam at 30mW/cm^2 is switched on at t=5s and off at t=30s in case of

DC161 and t=75s in case of MR. Photovoltage builds up slowly and takes over 60s to switch off. This behavior is in striking contrast with the observed nonlinear effect dynamics in DC161, where switching time is counted by tens of milliseconds. Hence, photovoltage generation is not responsible for observed holographic grating formation in DC161 doped devices.

MR samples give controversial results. In the SiOx aligned 10μm sample it was possible to register a large nonlinear effect on the time scale of photovoltage build-up. In PI aligned 10μm devices only the fast nonlinear effect (with efficiency only up to 0.08%) was observed. Such behavior correlates with the fact that SiOx is much more conductive then PI, also the photovoltage generated in MR doped samples with SiOx alignment is about 3 times larger.

This observation confirms that the choice of alignment is crucial for MR doped samples. By selecting proper alignment it is possible to select the mechanism we want to exploit in an MR doped system.

In C_{60} doped films the nonlinear effect is on the same timescale as observed for photovoltage build up. We believe that the observed photovoltage build up indicates that the dopant material is light sensitive and can produce charge (through ionic mechanisms or conductivity change) when excited by light. Photorefractive effect occurs due to the photo generated charge separation in conjunction with external DC field (around 1.5V) through the Carr-Helfrich effect.

Carr-Helfrich effect [7]

a) ***Charge separation through ions drift/diffusion***

b) ***Charge separation through conductivity changes***

This effect leads to reorientation of LC molecules in the resulting space charge field and usually takes place in the presence of a DC field. The field can be either applied externally or generated internally due to photovoltaic effect [3]. The formation of space charge is described [3] to have maximum resolution when the grating spacing is two times larger then the cell thickness. This effect takes place in the C_{60} doped sample and in the MR doped SiOx aligned sample.

There is no influence of DC fields up to Friedericksz threshold on the effect in DC161 doped samples. Such behavior suggests that the effect in DC161 doped films is not of ionic or space-charge origin.

Surface effects

Adsorption of the excited dye molecules on the alignment surfaces (persistent and permanent gratings)

This effect is found in MR and C_{60} doped devices in conjunction with some alignment agents promoting the adsorption on the surface [3]. We do not register any permanent or persistent components in the DC161 doped samples using light

intensities up to 1W/cm^2 for prolonged periods of time (even up to the melting point of 5CB) with or without application of external fields for all interfaces used (PI, SiOx, ZLI2222, PVA and pure glass). MR in conjunction with PI shows very good stability and does not form permanent or transient gratings even with very high optical powers (1W/cm^2). SiOx can give a persistent (lasting for hours or days) component at some conditions. For more detailed information on the alignment influence on the permanent component in MR doped films the authors would refer the reader to [4]. C_{60} has been reported to form permanent and persistent gratings [3]. We do not register this phenomenon with the alignments used (PI and ZLI2222).

Dynamic surface effect

Strongly depends on the alignment. This effect was described by Simoni et al in their studies of MR doped films [6]. We did not observe a similar effect in DC161 doped materials. We would like to emphasise that the dynamic surface effect time scale is of the order of seconds and does not agree with the observed holographic grating formation dynamics in DC161. It would be interesting to look at this effect in C_{60} doped materials, as they are also associated with adsorption on the surface of the samples.

Mechanisms leading to the change of the LC orientation or LC order parameter

Thermal effect

This effect is very likely to occur in highly absorbing MR and DC161 doped 5CB films. A lot of care has to be taken to separate the thermal contribution from the rest of the effects. Calculation of the temperature profile in dye-doped films is often very complicated and requires certain approximations. We will use the result from [8] to estimate maximum temperature rise in our samples, but for the explicit treatment of the problem the dynamic equation accounting for the periodicity of the optical field would have to be solved.

As calculated by Janossy [8]:

$$T_{stationary} = T_{ambient} + \frac{PA}{4\sqrt{\pi}k\omega_o} \qquad (1)$$

here A is the sample absorptance, $T_{stationary}$ and $T_{ambient}$ are the temperatures of the illuminated sample at thermal equilibrium and room temperature. P is the impinging beam power, k is thermal conductivity and w_o is the writing beam diameter. This relation is deduced for a Gaussian beam of a large diameter (w_o>>cell thickness), infinite substrates when the system has reached equilibrium. Periodicity of the field is not considered.

As calculated from (1), the maximum temperature rise in a 10μm 1% DC161 sample at light intensity 50mW/cm^2 and ambient temperature 22^{o}C, air cooling is 3.7^{o}C, which even for a narrow temperature-ranged 5CB is away from the isotropic transition temperature. The change of extraordinary refractive index with temperature (dn/dT)

in 5CB is of the order of 10^{-3} K^{-1} at 25°C [9]. At this temperature, one degree difference between the illuminated and non-illuminated regions may lead to a diffraction efficiency of 2.65% for the extraordinary and 0.13% for the ordinary beam. The temperature difference between illuminated and non-illuminated regions is not known, but from observation of many samples, we believe that the thermal effect is not the main mechanism leading to nonlinearity in our devices at light intensities under 100mW/cm^2. We start observing temperature effects in the discussed strongly absorbing 5CB systems at light intensities exceeding 200-300mW/cm^2 (depending on sample absorption). They are usually slow, of the order of seconds. The other important feature of the thermal effect is that it should depend on the overall absorbed energy and sample absorptance as in (1).

It is, therefore, interesting to note that the diffraction efficiency for both vertical and horizontal polarization of the probe beam correlates with absorptance (on the writing beam wavelength) normalized per unit length rather then simply absorbed energy. This comparison between absorptance and efficiency is obtained by measuring efficiency, reflection and transmission in tilted samples (in xz plane). Both, absorptance and normalized absorptance are shown on the fig.3 (using secondary axis at the right).

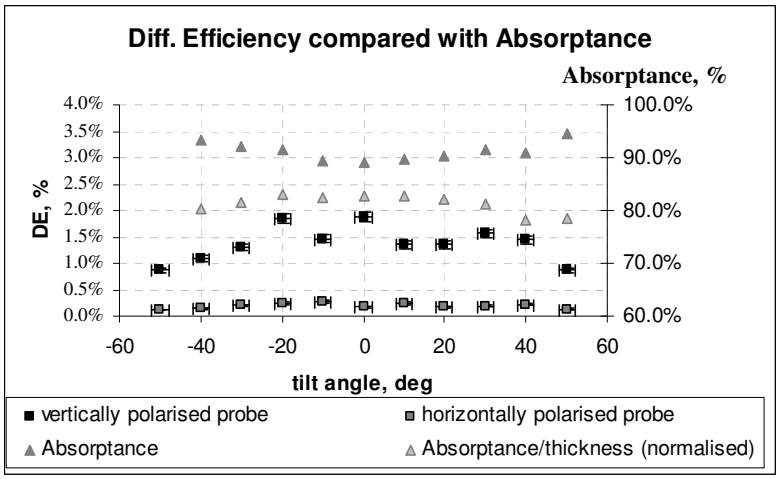

Fig. 3. The comparison between absorptance and efficiency in tilted 15μm 1%DC161 doped 5CB sample.

This fact is in agreement with the idea that the effect is due to the excitation of a dye molecule, transition of energy to surrounding LC molecules resulting in reorientation of the LC either through trans-cis isomerisation or the Janossy effect.

We expect thermal effects to be negligible in E7 and BLO48 doped samples.

Jánossy effect

This effect is due to the change in the interaction between excited dye molecules and the host leading to different torques experienced by LC molecules from excited species and resulting in its local reorientation. This effect is often observed in anthraquinone dyes, sometimes requiring external DC fields or focused light beams [2]. It is possible to find out whether this mechanism is responsible for the nonlinearity in the investigated systems based on the

assumption that in case of dye-host interaction mechanism, the effect will strongly depend on the host material (as in [2]).

We register almost no difference between performances of freshly doped E7 and BLO48. Unfortunately a more precise analysis will be possible only later, as with age the efficiency of materials changes in non-trivial fashion. DC161 devices dramatically improve with age, probably due to the fact that time is needed for these dopants to go into solution. Indeed, fresh samples viewed under the microscope show traces of undissolved dye, while samples that are 1-2 years old are uniform (fig.4). There is a correlation between the performance of the samples and their uniformity.

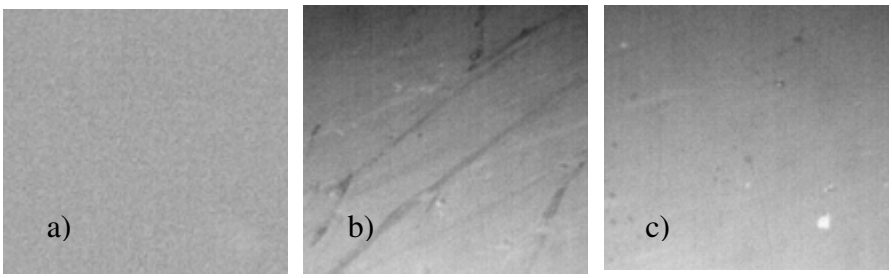

Fig. 4. 1% Dc161 samples under the polarised microscope.
a) sample built in 1987, 5CB; DE=0.29%;
b) freshly filled sample, E7; DE=0.02%;
c) sample filled 2 months ago, filtered, E7; DE=0.065%.

Trans-Cis transition upon photo-excitation in dye molecules

Consider simple 3 level model of azo dye molecule (fig. 5):

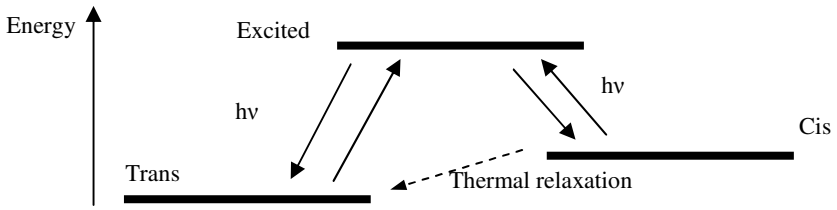

Fig. 5. Three-level energy model of the compound with trans and cis ground states.

Photochemical isomerisation in short can be described as excitation by light to the excited state and consequent relaxation from the excited state to trans or cis ground state by radiationless decay. For many systems there is approximately equal probability of forming cis- or trans- isomer. The most common situation is that when the isomer is irradiated at a particular wavelength the ratio of cis or trans compounds approaches a value that is characteristic for this wavelength - a photostationary state. The main factor governing the final ratio of isomers is the relative probability of exciting the ground state of each of the isomers. [10]

Trans isomers of dichroic dyes usually have lowest energy. They have elongated molecular shape and much higher order parameters in LC then cis species. These isomers behave as two different dyes [11] with different

absorption spectrums and different torques that they impose on the LC. The change of the geometrical shape of the dye when it undergoes the trans-cis transition leads to a change in the geometrical order of the surrounding LC molecules.

Dc161 dye has some unique features that distinguish it from other dyes that are used to enhance nonlinearity in LCs. The molecule is an anthraquinone derivative possessing two azo groups. Being an anthraquinone dye it has a high order parameter when dissolved in LC η=0.60 (confirmed by dichroic measurements). MR is an azo dye with quite high order parameter (η=0.48 confirmed by dichroic measurements). Azo groups' presence in both dopants and their symmetry suggest the possibility of trans- cis isomerisation.

Trans-cis transition is generally accompanied by change in absorption (trans and cis forms usually have different absorption spectra in polarised light). We do register the change of absorption in DC161 and MR doped samples upon illumination even in the case that the reorientation of the LC is fixed by the applied voltage (homeotropic sample, 45^o incidence, as in [11]).

Trans-cis transition can be very fast, and is in agreement with the dynamics of the observed effect. Geometrical orientation of the LC molecules can be studied by monitoring the refractive indexes of the sample. We perform the study of such reorientation.

4 Reorientation in DC161 doped NLC

4.1 Geometry and calculation

Let us consider two possible planes in which the LC director can move (fig.6). Such motion can be in the xy plane, the plane of the sample and will be characterised with the angle of reorientation θ. Another possible motion is in the xz plane and will result in the reorientation with the angle β. Using the setup on fig.1 we can measure the diffracted beam efficiency using two different polarisations of the reading beam. The diffraction efficiency is connected with the refractive index change by the following formula:

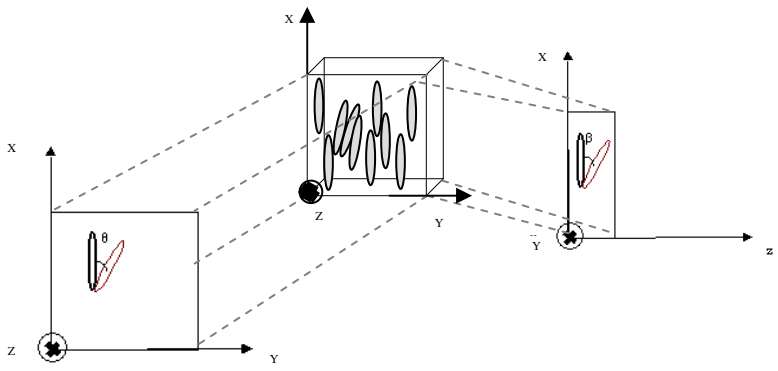

Fig. 6. Possible planes of director motion.

$$\eta = (J_1(\Delta\varphi)^2; \quad \Delta\varphi = \frac{2\pi d(n_{dark} - n_{illum})}{\lambda}. \tag{2}$$

Refractive index in the areas where reorientation occurs will have the following angular dependence:

$$n_{eff}^{\theta} = \frac{n_o n_{eff}^{\beta}}{\sqrt{n_o^2 \cos^2\theta + n_e^2 \sin^2\theta}} \qquad n_{eff}^{\beta} = \frac{n_o n_e}{\sqrt{n_o^2 \cos^2\beta + n_e^2 \sin^2\beta}} \tag{3}$$

This allows us to study reorientation in both planes. Both ∥ and ⊥ polarisation components of the reading beam will be sensitive to the in-plane reorientation (angle θ), while only the ∥ polarisation component of the reading beam will be sensitive to the out-of-plane reorientation (angle β). Information from the ⊥ component should be analysed first. It will give us the orientation change in the plane of a sample. The change in the angle θ will introduce change in both refractive indexes: the n∥ and n⊥. Knowing θ we can calculate the change in n∥ due to in-plane reorientation. Having accounted for reorientation in θ we can calculate β.

Of course, we will be able to see only the net effect of many LC molecules or molecular domains around dye molecules (1 dye molecule is surrounded by about 240 LC molecules for 1%wt concentration). Actual motion of each LC molecule might be much larger.

4.2 Experimental results

The diffraction efficiency of a 10μm 1%DC161 doped 5CB device is monitored for vertical and horizontal reading beam polarisations as a function of writing beam intensity. Diffraction build-up and relaxation dynamics is indicative of timescales of mechanisms responsible for the orientational change in a particular direction. Fig. 7 shows a typical dynamic behaviour of the diffracted signal for both reading beam polarisations. Build-up and relaxation times are almost identical in both cases, which leads us to the conclusion that the reorientation in both directions is triggered by the effects on the same time scale or one effect only. As can be seen from the fig. 7, at high light powers an overshoot appears, the nature of which is currently being investigated. The plausible explanation is that it takes longer to reach the equilibrium of trans-cis species at high light powers.

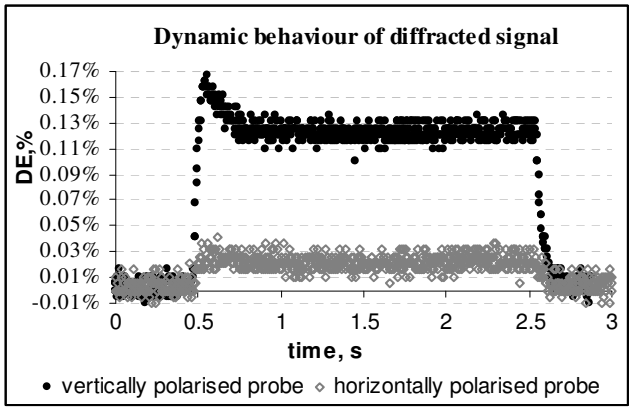

Fig. 7. Typical dynamic behaviour of diffracted signal for both polarisation of the reading beam, writing beams 40mW/cm^2

The direction of orientational change can be also derived from our experiment. From symmetry considerations in-plane reorientation does not have any preferred direction. Experiment shows that the relation between diffraction efficiencies of both orientations of

probe beam does not change as the sample is tilted in any direction, so the out-of-plane orientation is directed both, towards and away from the beam.

The reorientation angles are calculated using relations (2) and (3). The result of the calculation is shown on the fig. 8.

The reorientation angle is relatively small due to averaging over all molecules. The orientational effect saturates at a writing beam intensity of about 30mW/cm^2. The difference in the in plane and out of plane reorientation angles may be due to the difference in energy introduced by the anchoring on the alignment.

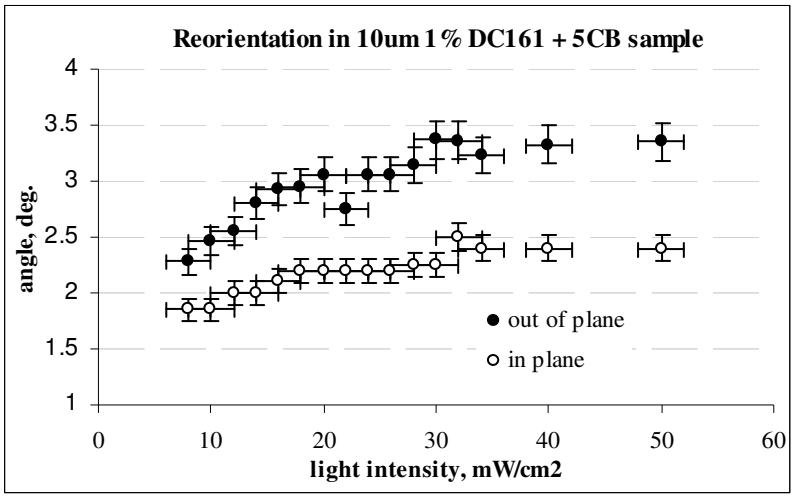

Fig. 8. Averaged molecular reorientation angles in 10μm 1%DC161 doped 5CB device.

Adding this information to the discussion of possible mechanisms in DC161, we suggest that the 3D director motion in these systems is triggered by the dopant undergoing a trans-cis transition with resulting change in macroscopic order parameter (possibly change in averaged orientation of domains around dye molecules with unchanged order parameter within such domain) as well as general change in the interaction between the dye and the host.

5 CONCLUSIONS

We investigate possible mechanisms in dopant-host systems in order to define what is responsible for the nonlinear effect in systems doped with three dopants: MR, C_{60} and DC161. The time scale of photorefractive effects, DC behaviour, dependence of the effects on the surface interface and host material, changes of absorption and refractive index are considered.

A note should be made, that with age the efficiency of materials changes in a non-trivial fashion. MR doped samples, as expected from ionic materials tend to give a decrease in efficiency while C_{60} and DC161 devices improve with age, probably due to the fact that the time is needed for these dopants to go into solution. This phenomenon prevented us from more detailed research on host influence, importance of the guest-host interaction and thermal effects.

Effect in C_{60} doped systems is attributed to photocharge formation and separation under the influence of a DC field. MR produces photovoltage and shows effects of ionic origin in conjunction with SiOx alignment.

The photorefractive-like effect in MR (PI aligned) and DC161 systems has trans-cis transition as an underlying mechanism possibly enhanced by the differences in the interaction of host with trans and cis isomers. Thermal effects might be present in the system, but they do not play an essential part in the holographic grating formation.

We measure the change of extraordinary and ordinary refractive index components of the device upon light illumination dynamically as a function of writing beams intensity through diffraction efficiency measurements. The reorientation angles are calculated from these measurements assuming the change of refractive index is caused by an orientational change. We find that molecules upon excitation follow a 3D trajectory. This molecular reorientation does not have preferred direction (away or towards the writing beam), has the same time characteristics in and out of plane. We believe that this is a macroscopic relative order- partial disorder transition but with easier motion in the out-of plane direction.

ACKNOWLEDGEMENTS

The authors are grateful to Gates Cambridge Trust for financial support and Dr. D Coates for fabricating dyes.

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